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Microscopical Analysis of Aerosols Collected in St. Louis, Missouri

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During twelve consecutive days of sampling, the TSP concentrations exceeded 75 $\mu g/m^3$ at the industrial site on ten days and nine days at the commercial site. The principal cause of high TSP concentrations, except for one sample from the industrial site, was the mineral calcite, which accounted for approximately 50% to 80% of the total TSP at both sites. Calcite particles were present at both sites as the primary component regardless of wind direction, suggesting that the source of these particles is pavement aggregate entrained by vehicles.

The highest TSP concentration--214.4 $\mu g/m^3$ recorded at the site near the industrial area--was the only sample that showed significant contributions from industrial sources. Approximately 60-75% of the TSP was due to coal and coke particles, probably produced for, or used in, metallurgical reduction. Another 5-15% of the TSP was composed of titanium dioxide and hydrated iron oxides, probably from pigment production.

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by

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The highest TSP concentration--214.4 $\mu g/m^3$ recorded at the site near the industrial area--was the only sample that showed significant contributions from industrial sources. Approximately 60-75% of the TSP was due to coal and coke particles probably produced for, or used in, metallurgical reduction. Another 5-15% of the TSP was composed of titanium dioxide and hydrated iron oxides, probably from pigment production.

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SECTION 1

INTRODUCTION

In July 1975 the Aerosol Research Branch of the U.S. Environmental Protection Agency conducted a special aerosol sampling study in St. Louis, Missouri to identify sources contributing to high concentrations of total suspended particulates (TSP) at two sampling locations. The first sampling site was on the roof of the four-story Municipal Courts (MC) building in downtown St. Louis at 14th and Market Streets. The second site was located approximately five miles south of MC on the roof of a three-story firehouse at the intersection of Broadway and Hurck (BH), adjacent to an industrial area. These sites are shown in Figure 1.

Daily hi-vol samples were collected from midnight to midnight from 15 July 1975 to 25 July 1975. Daily collections of aerosol samples were also made with an eight-stage Andersen impactor operated at one cfm. Uncoated, cellulose triacetate filters were used as collection substrates for all seven impactor stages plus the backup filter. The aerosol cut-off size, D_{50}, for each impactor stage is shown here in Table 1.

TABLE 1. IMPACTOR CUT SIZE, D_{50}

Stage	D_{50}, μm†
0	16.4
1	9.3
2	5.35
3	2.95
4	1.53
5	0.95
6	0.54
7	0.38
8	*backup filter

*The backup filter was a 0.8 μm pore size, cellulose triacetate membrane filter.

†D_{50} values for stages 2-6 determined by Flesch, et al.[1], others are calculated values

[1] J.P. Flesch, C.H. Norris and A.E. Nugent, "Calibrating Particulate Air Samplers with Monodispersed Aerosols: Application to the Andersen Cascade Impactor," Am. Ind. Hug. Ass. J., 28, 507-516, 1967.

SECTION 2

SAMPLE SELECTION AND ANALYTICAL METHODS

SAMPLE SELECTION

Several sampling days were chosen on the basis of their TSP concentrations and ratios (Table 2) for microscopical analysis. Those days with the highest, lowest, and average TSP concentrations at each site were selected for analysis. In addition, those days with the highest, lowest, and average TSP ratios for sites MC to BH were also selected for analysis. Unfortunately, 20 July 1975, which had the highest TSP ratio, and 21 July 1975, which had the highest TSP concentration, were not selected because impactor samples were not available for MC because of an electrical power failure at the site. The next highest TSP date (16 July) and TSP ratio date (22 July) which provided complete sample sets were substituted for 20 and 21 July. The 18 July 1975 sample was actually the closest to the arithmetic average TSP for site MC; however, the 22 July 1975 sample was selected for analysis since it was also close to the average TSP and also had the highest TSP ratio in the sampling.

High, low, and average TSP ratios in the set were sought because TSP ratios potentially represent the greatest variations between sites. The high and low TSP ratios can usually be attributed to a continuous local emission source near one site, coupled with extended wind persistence or calm. Occasionally, a high TSP ratio is caused by upset emissions from industrial processes, coupled with a wind direction that impacts the sampling site.

Episodes of highest and lowest TSP concentrations (not TSP ratios) at a site may be produced by area or regional sources such as sulfate or dust storm incidents. Therefore by using both TSP ratio and total TSP concentration as criteria for selecting sampling days, most of the sources contributing to TSP nonattainment are likely to be traced. Table 3 shows the samples selected for analysis and the resultant wind direction and speed on each date.

Analytical Approach

Small segments were cut from the hi-vol filters and impactor substrates and placed on glass slides containing individual puddles of a microscopical immersion liquid (n = 1.51). This immersion liquid clearly matches the refractive index of the glass fibers and the impactor membrane filters and serves to make these substrates transparent. A coverglass was then carefully placed over the oil-immersed segment to seal the surface against particle contaminants and to provide a plane surface for microscopical examination.

TABLE 2. TSP CONCENTRATIONS BY SITE

Sampling Dates, July 1975	Day of the Week	Mass Concentrations, µg/m³ MC	Mass Concentrations, µg/m³ BH	TSP Ratio, MC/BH
15	TUE	98.2	126.5§	0.78
16	WED	115.4†	139.2	0.83§
17	THU	115.4	171.1	0.67
18	FRI	88.4	183.9	0.48
19*	SAT	51.9	85.5	0.61
20*	SUN	95.0	64.4	1.48
21*	MON	118.4	80.8	1.47
22	TUE	99.8§	83.7	1.19†
23	WED	109.1	214.4†	0.51
24	THU	62.4	57.3‡	1.09
25	FRI	41.2‡	131.3	0.31‡
26	SAT	114.2	107.6	1.06
Arithmetic Average		92.5	120.5	0.87
Geometric Average		88.0	111.22	--

*Anderson impactor samples were not collected at the Municipal Court site due to an electrical power failure.

† Highest TSP or TSP ratio.

‡Lowest TSP or TSP ratio.

§Average TSP or TSP ratio.

TABLE 3. SAMPLES SELECTED FOR MICROSCOPICAL ANALYSIS

Municipal Court Site	Dates	Resultant Wind Direction	Wind Speed
Highest TSP	7/16	160°	7.8 mph
Lowest TSP	7/25	30°	5.5 mph
Average TSP	7/22	100°	4.2 mph
Broadway and Hurck Site			
Highest TSP	7/23	180°	8.5 mph
Lowest TSP	7/24	300°	5.7 mph
Average TSP	7/15	190°	6.4 mph
TSP Ratio MC/BH			
Highest	7/22	100°	4.2 mph
Lowest	7/25	30°	5.5 mph
Average	7/16	160°	7.8 mph

The mounted samples were examined by polarized light microscopy to identify the key particles by their optical and physical properties. The identified particles were grouped into one of five source categories: minerals, vehicle emissions, combustion products, biologicals, and miscellaneous. The total mass of all particles in a category was estimated as a percentage of the total mass of the sample--expressed as a numerical range--representing the confidence interval for the estimate. The concentration of individual particle types comprising a category was also estimated in a numerical range, designated by the letter code:

P = Primary (>25-100%)
M = Major (5-25%)
m = minor (0.5-5%)
t = trace (<0.5%)

These letter codes refer to the estimated concentrations of the entire sample, not just the category in which the particle types appear. For example, assume the mineral category has an estimated concentration of 75-90% of the total TSP. If the concentration of carbonates is listed as P (Primary, >25-100%), whereas all the other mineral types are t (trace, <0.5%), then carbonates are estimated to be present at a concentration of 75-90%.

When other particle types such as quartz and feldspars are present as m (minor, 0.5-5%), a mid-range value can be used for estimated percentage, and this can be subtracted from the total category estimate to obtain the Primary, P, percentage. In the example just presented, a quartz/feldspar content of m (0.5-5%) can be transformed into an average value of 3% and subtracted from the total mineral category estimate of 75-90%. Then the primary component, in this instance the carbonates, would have a value of 72-87%.

In some cases, letter concentration ranges are reported as t-m or m-M. These indicate that the numerical concentration is close to the upper limit of the trace concentration for t-m and also close to the upper limit for the minor concentration range for the m-M estimate.

There are several reasons for using letter categories for concentration estimates instead of numerical values. The main reason is that it is easier to compare component concentrations with a single letter code than with a number range. Therefore, it is also easier to spot the principal particle types contributing to the TSP problem. A letter code also emphasizes that the concentrations reported are estimates and not firm numerical values with known precisions.

It is, of course, possible to quantitate particle concentrations using stratified counting and sizing procedures along with appropriate particle density factors. However, this time-consuming approach could not be justified here since no mass weights (and therefore TSP concentrations) were obtained for the impactor samples. Also, hi-vols from only two days (23 July and 25 July) were available for microscopical analysis, so that the conclusions derived from the analyses are based mainly on impactor samples which do not capture proportionately as many large particles as the hi-vol samplers.

Selected segments of the impactor substrates were also mounted for scanning electron microscopy and x-ray microanalysis. Carbon-coated membrane filters provided electrical conductivity across the membrane surface so that substrate charging would not interfere with imaging.

Particle Type Descriptions

The mineral category groups particle types mainly by their generic mineral class or family, and occasionally as a specific mineral such as quartz. These minerals have numerous potential sources from soil to finished industrial product. Therefore, the minerals are assigned to a specific source only after the results of the sample analyses are complete. Then by a process of association with other particles and deduction based on source samples and meteorological data, the most probable sources can be identified.

The identification of particles in other categories is often synonomous with their source. Rubber tire fragments are readily recognized as dull, opaque, black, cigar-shaped particles that are impregnated with calcite from paved or unpaved road aggregate. Obviously it is not necessary to establish whether acrylonitrite-styrene-butadiene terpolymer or natural rubber is the source of these particles since they originate with vehicles. Most of the particles listed in the categories have identifying names associated with their source, e.g., flyash, oil soot, pollens, etc. The specific particle types included in each category are briefly described below.

Minerals

Quartz, feldspars are grouped together because of their usual common source--soil. Whereas quartz is a specific common mineral (α-SiO_2), the feldspars are a silicate group with the following end members: orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$). While the potassium feldspars are commonly present as orthoclase and microcline, they are minor components compared to quartz. Though the optical properties of these minerals are distinctive enough to separate them from other mineral classes, the feldspars have closely similar optical properties that allow these minerals to be grouped together.

Carbonate group is dominated by calcite ($CaCO_3$) and less frequently, dolomite ($CaMg[CO_3]_2$), the two most commonly used minerals in paved and unpaved road aggregate. In most urban areas studied by IIT Research Institute (IITRI), the predominant source of calcite and/or dolomite has been paved road aggregate. It has become a somewhat common practice to describe particles emitted from paved roads as resuspended dust. The term 'resuspended' implies that particles deposited onto the roadway from sources other than vehicular traffic were suspended by vehicular traffic. Since more than 90% of the sub-100 μm particles on paved roads are merely fragments of the pavement aggregate, we have opted to drop the prefix re and describe these vehicle-generated particles as suspended dust. This may aid in clarifying the source of those minerals that create most of the TSP nonattainment problems.

Micas are a group of mineral silicates that are seen as distinctive, thin flakes on aerosol filters. Muscovite [$KAl_2(AlSi_3O_{10})(OH)_1$] and biotite $(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3$ the two most common micas, can usually be traced to soil, though they also occur when igneous rocks are used as aggregate for paved or unpaved roadways.

Clay is a rock term and usually applies to a number of minerals that are predominately hydrous aluminum silicates. The particles usually occur as agglomerates of submicrometer to 5 micrometer single crystals.

Iron oxides are grouped with the minerals because many iron oxides are formed by mineral weathering. Iron oxides from industrial sources such as integrated steel mills consist principally of hematite (α-Fe_2O_3), magnetite (Fe_3O_4) wustite (FeO), and, infrequently, metal flakes. The iron oxides from mineral weathering are mainly the hydrated iron oxides goethite and limonite, though hematite is also found. The iron oxides listed under minerals are usually seen as small particles adhering to the larger soil grains of quartz and feldspars.

Vehicle Emissions

Vehicle--auto and truck--emissions principally consist of sub-0.1 micrometer amorphous elemental carbon particles that form chainlike agglomerates approximately 0.5-0.9 μm in diameter. Of these exhaust pipe emissions, about 10% are lead compounds, mainly halides and oxides. Vehicle combustion emissions from gasoline and diesel are estimated from the submicrometer, black opaque particles. It is possible to apply source coefficient factors to compare the lead concentration, determined spectroscopically, to the carbon content. However, the source coefficient factor for Pb/C has been estimated anywhere from 1:1 to 1:10. Therefore, applying these factors is sheer guesswork and unreliable compared to microscopical estimates.

Rubber tire fragments are produced by autos (largely synthetic) and trucks (partially natural rubber). The particles are usually longer than 10 μm and have shape profile ratios that range from 3:1 to 7:1.

Combustion Products

Flyash derived from coal combustion consists of four components: glassy spheres, partially fused opaque minerals, iron oxides (mostly magnetite), and partially combusted coal. All but the partially combusted coal fragments are included in this particle source category. While magnetite is also found in steel mill emissions, trace quantities of spherical, fused magnetite are normally ascribed to the more abundant source--either flyash from coal combustion or nonmagnetic iron oxides from steel production. The fused magnetite from coal combustion is usually greater than 5 μm in diameter, while those from steel mills are less than 5 μm in diameter. Nonspheroidal magnetite is excluded from this category.

Coal and coke fragments are presented as a separate category because the concentrations found in certain samples at the BH site far exceeded that

associated with flyash. More than 90% of these particles were coke fragments rather than raw coal.

Partially combusted plant parts are most likely the structural residues from coal pyrolysis rather than emissions from urban or industrial incinerators.

Oil soot is the carbonaceous cenosphere from the pyrolysis and incomplete combustion of sprayed oil droplets.

Submicrometer ammonium sulfate and nitrate are grouped together simply because they are usually secondary aerosols from hydrocarbon fuel combustion. The quantities of sulfates and nitrates appeared similar at both sites on each day so that the sources appear to be areawide.

Biologicals

With the exception of starch, which was mainly cornstarch, the pollens, spores, conidia, plant fragments, and insect parts, are natural background aerosols. Because cornstarch is so widely used by industry and may also be emitted in substantial quantities during loading for transport, starch may be considered an industrial emission.

Micellaneous

Titanium dioxide and hydrated iron oxides were frequently found at the BH site as 3-20 μm agglomerates of submicrometer particles. While each was found in the same sample, they always occured separately. That is, the titanium dioxide and hydrated iron oxide particles were never present in the same agglomerated particle.

Since each agglomerate was also free of any other particle type, it appears that these agglomerates were emitted as final products, probably from pigment manufacturing. It is especially important to note that the hydrated iron oxide were unique and easily distinguishable from iron oxides from steel mill, flyash, or soil sources.

Magnetic fragments included nonspheroidal metals and metal oxides that responded to movements of a small magnet held close to the microscope stage. In some cases these magnetic fragments appeared as slivers, perhaps from wear or erosion of suspension systems from autos and trucks.

SECTION 3

SAMPLE ANALYSES AND RESULTS

After analyzing the four available hi-vol filters it was apparent that industrial emissions were inundating the BH site when southerly winds prevailed. Therefore, our results are grouped in this section according to two wind directions: southerly and other.

The results of the microscopical analysis of the hi-vol filters are presented in Table 4 and the microscopical analysis of the impactor samples in Tables 5A-E and 6A-E. The data are discussed by sampling date and site.

ANALYTICAL RESULTS FOR SOUTHERLY WIND DIRECTIONS

23 July 1975

Resultant Wind Direction:	180
Resultant Wind Speed:	8.5 mph

This day produced the highest TSP concentration at the BH site and the fifth highest TSP concentration at MC. Coke and coal fragments accounted for 60-75% of the sample mass (Figure 2). These coke and coal concentrations were higher in this sample than any other analyzed and were the main cause of the high TSP. Agglomerates of submicrometer, yellow birefringent, high refractive particles (Figure 3), along with similar white agglomerates, contributed 5-15% of the TSP. These agglomerates were later identified as oxides.

Broadway and Hurck (214.4 $\mu g/m^3$)

On days of southerly wind, significant amounts of these oxides were present at BH, with significantly smaller amounts at MC. The two agglomerates were never found joined or intermixed. Despite their morphological similarities, they were present in different proportions with respect to each other from day to day, which indicates generation by separate processes. Both agglomerates were identified with scanning electron microscope (SEM) and x-ray microanalysis. The yellow oxide contained iron (Figures 4 and 5). Based on this analysis, color, and birefringence, these agglomerates were hydrated iron oxide, probably goethite. The white agglomerates contained titanium and based on the optical properties of the particles were titanium dioxide (Figures 6 and 7).

Other industrial emissions such as flyash and ammonium sulfate were trace sample components.

TABLE 4. AEROSOL COMPOSITION AND SIZE RANGE OF HI-VOLUME FILTER PARTICLES

	23 July						25 July					
	Municipal Court			Broadway & Hurck			Municipal Court			Broadway & Hurck		
	Est. wt %	Geometric size, μm average	range	Est. wt %	Geometric size, μm average	range	Est. wt %	Geometric size, μm average	range	Est. wt %	Geometric size, μm average	range
Minerals	75-90			15-25			90-95			70-85		
quartz, feldspars	m	15	<1-40	t-m	15	<1-40	m	12	<1-60	m	15	<1-35
carbonates	P	6	<1-32	M	7	<1-40	P	8	<1-45	P	6	<1-35
micas	t	12	5-60	t	15	5-50	t	15	5-45	t	15	5-100
clays	t	<1	<1	t	<1	<1	t	<1	<1	t	<1	<1
iron oxides	t	7	<1-10	t	<1	<1	t	3	<1-30	t	3	<1-20
Vehicle Emissions	5-10			<2			1-5			<2		
carburetor tailpipe exhaust	m	<1	<1	m	<1	<1	t-m	<1	<1	t	<1	<1
rubber tire fragments	m	30	5-100	t	20	5-80	m	25	5-100	t	30	5-100
Combustion Products	5-15			60-75			1-2			10-20		
fly ash	t	5	<1-12	t-m	5	<1-25	t-m	6	<1-18	m	6	→25
coal and coke fragments	m-M	6	<1-50	P	10	<1-100	t	8	<1-70	M	15	→110
partially combusted plant parts	t	35	→100	t	60	→80	t	40	→70	t	60	→400
oil soot	t	30	→50	t	15	→50	t	15	15-50	t	15	→65
ammonium sulfate	m	<1	<1	t	<1	<1	t	<1	<1	m	<1	<1
Biologicals	<1			<1			<1			<1		
pollens, spores conidia	t	30	6-110	t	25		t	30	→70	t	35	→90
plant fragments	t	40	5-100	t	100	→240	t	50	→160	t	60	→240
starches	t	12	8-16	t	10		t	12	→18	t	15	
insect parts	t						t	80		t		→700
Miscellaneous	<1			5-15						<1		
titanium dioxide	t	1	1	t-m	1	1				t	<1	<1
hydrated iron oxides	t	1	1	M	1	1				t	<1	<1
magnetic fragments	t	10	7-16	t	6	3-20				t	7	
TOTAL SUSPENDED PARTICULATES (μg/m³)		109.1			214.4			41.2			131.3	

P = primary (>25)
M = major (5-25)
m = minor (0.5-5)
t = trace (<0.5)

TABLE 5A. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE MUNICIPAL COURT SITE ON 15 JULY

Components	Estimated Weight Percentage, impactor stage 0	1	2	3	4	5	6	7	8
Minerals	85-95	85-95	85-95	80-95	75-90	50-65	30-40	5-10	1-5
quartz, feldspars	m	m	m	m	m	t	t	t-m	m
carbonates	P	P	P	P	P	P	P	M-P	m
micas	m	m	m	m	t				
clays	t	t	t	t	t				
iron oxides	t	t	t	t	t	t	t	t	
Vehicle Emissions	1-5	1-5	<1	<1	1-2	10-20	25-40	25-40	80-90
carburetor tailpipe exhaust	t	t	t	t-m	m	M	P	M-P	P
rubber tire fragments	m	m	t	t					
Combustion Products	5-10	5-10	5-10	5-10	5-15	20-30	20-30	50-65	1-10
fly ash	t	t	t	m	m	t			
coal and coke fragments	m-M	t-m	m-M	m	M	M	M	t	m
partially combusted plant parts	t	t	t	t					
oil soot	m	t-m	t-m	t	t	t			
ammonium sulfate								P	t
Biologicals	∿1	∿1	∿1	∿1	<1				
pollens, spores conidia	t	t	t	m	t				
plant fragments	t	t	t	t	t				
starches	t	t	t						
insect parts	t	t		t					
Miscellaneous	∿1	1-2	<1	1-5	5-10	5-15	1-10	<1	
titanium dioxide	t	t	t	m	M	m-M	m	m	
hydrated iron oxides	t	t	t	m	m	m	m	m	
magnetic fragments	t	t	t						
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					98.2				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

TABLE 5B. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE MUNICIPAL COURT SITE ON 16 JULY

Components	Estimated Weight Percentage impactor stage 0	1	2	3	4	5	6	7	8
Minerals	85-95	90-95	>95	>90	85-95	55-70	5-10	1-5	1-5
quartz, feldspars	m	m	m	m	m	m	t	t	t
carbonates	P	P	P	P	P	P	M	m	t
micas	m	m	m	m	t	t		t	t
clays	t	t	t	t					t
iron oxides	t	t	t	t	t	t			t
Vehicle Emissions	1-5	1-5	<1	∿1	1-5	20-35	20-35	20-35	80-90
carburetor tailpipe exhaust	t	t	t	m	m	M-P	M-P	P	
rubber tire fragments	m	m	t						
Combustion Products	1-5	1-2	1-2	1-5	5-10	10-20	55-70	65-80	5-15
fly ash	t	t	t	m	t				
coal and coke fragments	m	t	m	m	m	M	m	t	m
partially combusted plant parts	t	t		t					
oil soot	t	t	t	t	t				t
ammonium sulfate							P	P	t
Biologicals	<1	<1	<1	∿1	<1				<1
pollens, spores conidia	t	t	t	m	t				t
plant fragments	t	t	t	t	t				
starches	t	t		t					
insect parts									
Miscellaneous	<1	<1							
titanium dioxide	t								
hydrated iron oxides									
magnetic fragments	t	t							
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					115.4				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

TABLE 5C. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE MUNICIPAL COURT SITE ON 22 JULY

Components	Estimated Weight Percentage, impactor stage 0	1	2	3	4	5	6	7	8
Minerals	85-90	90-95	90-95	90-95	90-95	65-80	5-15	1-5	1-5
quartz, feldspars	M	m	m	m	m	m	m	t	t
carbonates	P	P	P	P	P	P	P	m	m
micas	t	t	t	t-m	t				
clays	t	t	t	t	t				
iron oxides	t	t	t	t-m	M	M	m	t	
Vehicle Emissions	5-10	1 2	1-2	1-5	5-10	15-25	30-45	25-40	90-95
carburetor tailpipe exhaust	t	t	t-m	m	m-M	M	P	P	P
rubber tire fragments	m-M	m	t						
Combustion Products	1-5	1-5	1-5	1-5	1-5	5-10	50-65	60-75	1-5
fly ash	t	t	t	t	t				
coal and coke fragments	m	m	m	m	m	M	t	t	m
partially combusted plant parts	t		t	t	t				
oil soot	t	t	t	t	t	t			
ammonium sulfate	t-m		m	t			P	P	
Biologicals	∿1	<1	∿1	<1	<1				<1
pollens, spores conidia	t-m	t	t-m	t	t				t
plant fragments	t	t	t	t					
starches	t-m	t	t	t					
insect parts	t		t	t	t				
Miscellaneous	<1	<1	<1	∿1	∿1	<1	<1		
titanium dioxide		t					t		
hydrated iron oxides	t	t	t	t	t	t			
magnetic fragments	t		t	t	t				
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					99.8				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

TABLE 5D. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE MUNICIPAL COURT SITE ON 23 JULY

Components	Estimated Weight Percentage, impactor stage 0	1	2	3	4	5	6	7	8
Minerals	85-90	90-95	90-95	85-95	85-95	65-80	20-35	20-30	1-5
quartz, feldspars	M	M	M	m-M	m	m	m	m	m
carbonates	P	P	P	P	P	P	M-P	M-P	m
micas	m	m	m	t					
clays	t	t	t						
iron oxides	t	t	t	t	t	m	t	t	
Vehicle Emissions	1-5	∿1	∿1	∿1	1-5	5-10	10-20	10-20	85-95
carburetor tailpipe exhaust	t	t	t	m	m	M	M	M	P
rubber tire fragments	t-m	t	t	t					t
Combustion Products	1-5	1-5	1-5	1-5	5-10	15-25	55-70	60-75	1-5
fly ash	t	t	t	t-m	t				
coal and coke fragments	m	m	m	m	m-M	M	m	m	m
partially combusted plant parts	t	t	t	t	t				
oil soot	t	t	t	t	t				
ammonium sulfate							P	P	m
Biologicals	<1	<1	<1	<1-2	<1				
pollens, spores conidia	t	t	t	t-m	t				
plant fragments	t	t	t						
starches	t	t	t	t					
insect parts			t	t					
Miscellaneous	<1-2	∿1	<1-5	1-5	1-5	1-5			
titanium dioxide	t	t	t	t					
hydrated iron oxides	t-m	t	m	m	m	m			
magnetic fragments	t								
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					109.1				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

TABLE 5E. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE MUNICIPAL COURT SITE ON 24 JULY

Components	Estimated Weight Percentage impactor stage 0	1	2	3	4	5	6	7	8
Minerals	80-90	90-95	90-95	90-95	85-95	75-90	50-65	20-35	1-5
quartz, feldspars	M	M	M	M	M	M	M-m	m	m
carbonates	P	P	P	P	P	P	P	P	M
micas	m	m	m	m	m				
clays	t	t	t	t	t				
iron oxides	t	t	t	t	t	t	t	t	
Vehicle Emissions	5-10	1-5	∿1	∿1	1-5	5-10	25-40	40-50	90-95
carburetor tailpipe exhaust	t-m	t	t	t	m	M	P	P	
rubber tire fragments	m-M	m	t	t					
Combustion Products	1-5	1-5	1-5	1-5	1-5	5-15	5-15	25-40	1-5
fly ash	t	t	t-m	m	m				
coal and coke fragments	m	m	m	t-m	m	M	M	M	M
partially combusted plant parts	t								
oil soot	t				t				
ammonium sulfate	t	t					t	M	t
Biologicals	<1	<1	<1-2	<1	<1	<1			
pollens, spores conidia	t	t	t	t	t	t			
plant fragments	t		t						
starches	t	t	t						
insect parts				t					
Miscellaneous			<1	<1	<1				
titanium dioxide			t	t	t				
hydrated iron oxides									
magnetic fragments									
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					62.4				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

TABLE 6A. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE BROADWAY AND HERCK SITE ON 15 JULY

Components	Estimated Weight Percentage, impactor stage 0	1	2	3	4	5	6	7	8
Minerals	70-85	55-70	60-75	55-70	30-45	1-5	1=2	1	5-10
quartz, feldspars	M	m-M	m	m	m	t	t	t	m
carbonates	P	P	P	P	P	m	m	t	M
micas	t	m	m	m	t				
clays	t	t	t	t	t	t	t		
iron oxides	t	t	t	t	t	t	t	t	
Vehicle Emissions	1-5	∿1	∿1	<1	∿1	10-20	10-20	20-35	75-85
carburetor tailpipe exhaust	t	t	t	t	t	m-M	M	M	P
rubber tire fragments	m	t	t	t	t				m
Combustion Products	15-25	25-40	25-40	25-40	25-40	5-10	15-25	60-75	10-20
fly ash	t	t-m	t-m	t-m	t				
coal and coke fragments	M	P	P	P	P	m	m	m	m-M
partially combusted plant parts	t	t	t	t	t				
oil soot	t	t	t	t	t	t			
ammonium sulfate						m	M	P	m-M
Biologicals	<1	<1	∿1	∿1	∿1				
pollens, spores conidia	t	t	t	t	t				
plant fragments	t	t	t	t	t				
starches	t	t	t	t	t				
insect parts	t	t	t	t	t				
Miscellaneous	1-5	1-10	1-5	5-10	30-45	70-85	65-75	5-10	
titanium dioxide	m	m	m	m	M	P	P	P	
hydrated iron oxides	t	m	m	m	M	P	P	M	
magnetic fragments	t	t	t	t	t				
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					126.5				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

TABLE 6B. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE BROADWAY AND HERCK SITE ON 16 JULY

Components	Estimated Weight Percentage impactor stage 0	1	2	3	4	5	6	7	8
Minerals	70-85	65-80	60-75	70-85	30-45	1-5	1-5	<1	1-5
quartz, feldspars	M	M	m-M	m	m	m	t	t	t-m
carbonates	P	P	P	P	M	m	m	t	t-m
micas	m	m	m	t	t				
clays	t	t	t	t					
iron oxides	t	t	t	t	t		t		t
Vehicle Emissions	1-5	<1	1-2	1-2	2-5	10-25	10-25	30-45	55-70
carburetor tailpipe exhaust	t	t	t-m	m	m	M	M	P	P
rubber tire fragments	m	t	t						t-m
Combustion Products	10-25	20-35	15-25	10-20	45-60	55-70	55-70	55-70	20-30
fly ash	t	t	t	t	t				
coal and coke fragments	M	M-P	M	M	M-P	M	m	m	M-P
partially combusted plant parts	t	t	t	t	t				
oil soot	t	t	t	t					
ammonium sulfate						t-m	P	P	t
Biologicals	<1	<1	<1	<1					
pollens, spores conidia	t	t	t	t					
plant fragments	t	t	t						
starches	t	t							
insect parts	t		t						
Miscellaneous	1-5	1-5	10-20	5-15	5-10	5-15	5-15	<1	<1
titanium dioxide	t-m	m	M	m-M	M-P	P	P	m	t
hydrated iron oxides	t	t	t	t-m	t-m	m	m	t	t
magnetic fragments	t	t	t		t				
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					139.2				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

TABLE 6C. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE BROADWAY AND HERCK SITE ON 22 JULY

Components	Estimated Weight Percentage impactor stage 0	1	2	3	4	5	6	7	8
Minerals	85-95	85-95	90-95	90-95	85-95	45-60	1-2	1-5	5-10
quartz, feldspars	M	m-M	t-m	t-m	t-m	t-m	t	t	t-m
carbonates	P	P	P	P	P	P	M	m	m
micas	m	m	t-m	t	t				
clays	t	t	t	t	t	t			
iron oxides	t	t	t	t	t				
Vehicle Emissions	1-5	<1	<1	∿1	1-5	10-20	20-35	20-35	80-90
carburetor tailpipe exhaust	t	t	t	t	m	M	P	P	P
rubber tire fragments	m	t	t	t					
Combustion Products	1-5	1-5	1-5	1-10	1-5	30-45	55-70	65-80	5-10
fly ash	t	t	t	t					
coal and coke fragments	m	m	m	m-M	m	M	m		m
partially combusted plant parts	t	t	t	t					
oil soot	t	t	t	t					
ammonium sulfate							P	P	t
Biologicals	<1	∿1	∿1	∿1	<1	<1			
pollens, spores conidia	t	m	t-m	t	t				
plant fragments	t	t	t	t	t				
starches	t	m	t	t	t	t			
insect parts		t	t	t	t				
Miscellaneous	<1	<1	<1	<1	<1				
titanium dioxide	t	t							
hydrated iron oxides	t	t							
magnetic fragments	t	t	t	t	t				
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					83.7				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

TABLE 6D. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE BROADWAY AND HERCK SITE ON 23 JULY

Components	Estimated Weight Percentage impactor stage 0	1	2	3	4	5	6	7	8
Minerals	50-65	45-60	45-60	40-55	25-40	5-10	1-5	1-5	1-5
quartz, feldspars	M	M	M	M	m	m	m	t	t
carbonates	P	P	P	P	M-P	M	m	m	t-m
micas	t	t	t	t					
clays	t	t							
iron oxides	t	t	t	t	t				
Vehicle Emissions	∿1	<1	<1	<1	∿1	10-20	10-25	30-50	90-95
carburetor tailpipe exhaust	t	t	t	t	t-m	M	M	P	P
rubber tire fragments	t	t							
Combustion Products	35-50	40-55	35-50	40-55	55-70	65-80	65-80	50-65	1-5
fly ash	t	t	t	t					
coal and coke fragments	P	P	P	P	P	P	P	M	m
partially combusted plant parts	t			t					
oil soot	t		t						
ammonium sulfate	t						P	P	t
Biologicals	<1	<1	<1	<1	<1				
pollens, spores conidia	t	t	t	t	t				
plant fragments		t	t	t	t				
starches	t								
insect parts		t		t	t				
Miscellaneous	1-5	5-10	5-15	5-15	5-15	5-15	1-10	1-5	
titanium dioxide	t-m	m	m	M	m	m	t-m	t-m	
hydrated iron oxides	m	M	M	M	M	M	m-M	m	
magnetic fragments	t			t					
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					214.4				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

TABLE 6E. AEROSOL COMPOSITION BY IMPACTOR STAGE FOR THE BROADWAY AND HERCK SITE ON 24 JULY

Components	Estimated Weight Percentage, impactor stage 0	1	2	3	4	5	6	7	8
Minerals	85-95	90-95	90-95	90-95	85-95	70-85	45-60	35-50	1-5
quartz, feldspars	M	M	M	M	M	M	M	m	m
carbonates	P	P	P	P	P	P	P	M	m
micas	t	t	m	t	t				
clays	t	t	t	t	t				
iron oxides	t		t	t	m	t	t		
Vehicle Emissions	1-5	<1	∿1	<1	1-2	5-10	40-50	30-45	75-85
carburetor tailpipe exhaust	t	t	t	t	M	M	M	M	P
rubber tire fragments	m	t	t		t				
Combustion Products	1-5	1-5	1-5	1-5	1-5	10-20	10-20	25-40	15-25
fly ash	t	t	t	t	t				
coal and coke fragments	m	m	m		m-M	M	m-M	m	M
partially combusted plant parts	t	t		t					
oil soot	t	t							
ammonium sulfate	t			t		t	m	P	
Biologicals	<1	<1	∿1	<1	<1				
pollens, spores conidia	t	t	t-m	t-m	t				
plant fragments	t	t	t	t	t				
starches	t	t	t						
insect parts			t		t				
Miscellaneous	∿1	<1	<1		<1				
titanium dioxide	t	t	t						
hydrated iron oxides	t	t			t				
magnetic fragments	t								
TOTAL SUSPENDED PARTICULATES ($\mu g/m^3$)					57.3				

P = primary (>25%) M = major (5-25%) m = minor (0.5-5%) t = trace (<0.5%)

Roadway minerals, primarily calcium carbonate particles, contributed most of the remaining mass, about 15-25%. Vehicle emissions were present in trace amounts.

Impactor stages 0-3 contained the same components, though the modal size decreased from about 12 μm for stage 0 to about 4 μm for stage 3. Figure 8 shows an impaction spot on stage 2 and Figure 9 a spot from stage 3. The bright white particles are calcium carbonate minerals, which constituted about half of the sample mass on these stages. Most of the rest of the mass is composed of coal and coke fragments, which, as noted for the hi-vol sample, were present at a higher concentration than on any other sample analyzed. Up to 15% of this sample is composed of titanium oxide and hydrated iron oxide, with the iron oxide predominating on all four upper stages. These oxides can be seen in Figure 8 as the large, dark gray, irregular particles scattered throughout the sample.

Stage 2 was examined by scanning electron microscope (Figure 10). An electron beam area scan produced an x-ray spectrum (Figure 11) with peaks for aluminum, silicon, calcium, titanium, and iron. The aluminum and silicon are present primarily in soil minerals such as quartz, feldspars, and micas, whereas the calcium occurs in calcite. Both the titanium and iron are present mainly as TiO_2 and $Fe_xO_y \cdot nH_2O$, respectively, while the iron also occurs in other mineral particles as a minor component.

Stage 4 (Figure 12) had basically the same composition as stages 0-3 but showed an increase in the percentage of coal and coke fragments and a decrease in the mineral concentration. Direct vehicle emissions were still trace sample components. The modal size of all particles was approximately 2 μm.

About 65-80% of the mass on stage 5 (Figure 13) was coal and coke fragments. Vehicle exhaust composed 10-20% of the mass, with some titanium dioxide and hydrated iron oxide present and a minor amount of minerals.

Industrial emissions were the predominant component of the sample on stage 6, consisting of coal and coke fragments and ammonium sulfate. The $(NH_4)_2SO_4$ formed large birefringent crystals on the filter (Figure 14). Vehicle exhaust was present in this sample in about the same proportion as on stage 5. The modal particle size for stage 6 was 1 μm.

About half the sample mass on stage 7 (Figure 15) was recrystallized ammonium sulfate, with the balance contributed by vehicle exhaust (35-50% of the total) and coal and coke fragments. Traces of minerals titanium dioxide and hydrated iron oxide were also present. The x-ray area scan of an impaction spot on this stage (Figures 16 and 17) shows that sulfur is the primary element present with some calcium, titanium, and iron, and traces of Al, Si, Cu, and Zn. The large, angular, dark gray to black plates at the periphery of the impaction spot contain sulfur, which partially corroborates the optical identification of ammonium sulfate.

The backup filter had an even background of tailpipe exhaust. There were traces of almost every type of particle found on the upper stages.

Municipal Court (109.1 μg/m³)

While the hi-vol sample collected at BH had the highest TSP concentration during this study, the hi-vol at MC recorded only the fifth highest TSP concentration at that site. Calcium carbonate particles were the primary components of this high-volume sample (Figure 18). Most of these minerals were less than 10 μm in diameter and were probably raised by automobile traffic. When the direct mobile emissions such as carbonaceous tailpipe exhaust (a large portion of the background urban aerosols) and rubber tire fragments are included with the minerals, the aerosols from automobile traffic composed 85-95% of the total sample mass.

The southerly wind on this sampling day placed this site downwind of an industrial area of the city. Industrial emissions contributed 5-15% of the mass loading, primarily coal and coke fragments, plus ammonium sulfate. There were traces of titanium dioxide and hydrated iron oxides, flyash, and oil soot. Biological particulates were also trace sample components.

Impactor stages 0-4 were almost identical in composition, though the modal size decreased from about 10 μm for stage 0 to about 2 μm for stage 4. Photomicrographs of stages 2, 3, and 4 are shown in Figures 19, 20, and 21, respectively. Calcium carbonate minerals with some quartz, feldspar, and mica constituted 85-95% of the sample mass on these stages. The remaining mass was from industrial emissions, primarily coal and coke fragments. The industrial emissions were similar to those found at BH, though in significantly smaller concentrations. Some of the titanium dioxide and hydrated iron oxide agglomerates (<5% of the sample mass) and a small amount of rubber tire fragments were present on stages 0 and 1 and vehicle exhaust particles on stages 3 and 4.

Stage 5 (Figure 22) showed an increase in vehicle exhaust particles to 5-10% and coal and coke fragments to 15-25% of the sample mass. Titanium dioxide and hydrated iron oxide agglomerates were present in about the same concentration as on stage 4. The remainder was primarily calcium carbonate minerals. The modal size for particles on this stage was about 1 μm.

The concentration of vehicle exhaust particles doubled from stage 5 to stage 6. Stage 6 (Figure 23) also showed a reduction in the concentration of minerals to 20-35%. These minerals were almost entirely calcite. Ammonium sulfate crystals were first present in appreciable quantities on this stage and accounted for most of the 55-70% of the mass from industrial emissions. The balance of industrial emissions was coal and coke fragments. The modal size for particles on this stage was less than 1 μm.

The primary component on stage 7 was recrystallized ammonium sulfate (Figure 24). These sulfates appear as large, birefringent crystals which are most easily seen with crossed polars because refractive indices are close to those of the immersion liquid. Vehicle tailpipe exhaust particles were the other predominant sample component. The modal particle size for this impactor stage was less than 1 μm.

The backup filter had a fine background of elemental carbon from vehicle exhaust and also contained traces of most particulates encountered on the upper stages.

16 July 1975

Resultant Wind Direction: 160°
Resultant Wind Speed: 7.8 mph

The second highest TSP concentration at MC and the second highest TSP concentration at BH both occurred on 16 July 1975. The TSP ratios for MC/BH for this day (0.83) were closest to the average for all the days (0.87). Hi-vol filters were not available for microscopical analysis from either site on this date.

Broadway and Hurck (139.2 μg/m³)

The particles on this set of impaction substrates were very similar to those collected on 23 July 1975. The major difference was that the coal and coke fragments constituted a smaller percentage of this sample, while the mineral concentration was greater (Tables 5A-E and 6A-E). The titanium dioxide and hydrated iron oxide accounted for the same proportion of the sample as on 23 July 1975, but titanium dioxide was the predominant agglomerate instead of hydrated iron oxide.

Municipal Court (115.4 μg/m³)

This set of impactor samples showed a particulate distribution very similar to that described for the 23 July 1975 samples. There were, however, almost no titanium dioxide or hydrated iron oxide agglomerates present on any of the stages except for traces on stages 0 and 1. Coal and coke fragments were present at a slightly lower level than on the 23rd. Industrial sources collectively contributed less than 10% of the total sample mass. The dominant cause of the high TSP was calcite, most probably from paved road aggregate suspended by vehicular traffic.

15 July 1975

Resultant Wind Direction:	190°
Resultant Wind Speed:	6.4 mph

This sampling date produced a TSP concentration at the BH site (126.5 $\mu g/m^3$) that was closest to the average for that site (120.5 $\mu g/m^3$). The MC site also had a TSP concentration (98.2 $\mu g/m^3$) that was close to the site average (92.5 $\mu g/m^3$). No hi-vol filters were available for microscopical analysis.

Broadway and Hurck (126.5 $\mu g/m^3$)

These impactor samples were also similar to those collected on 16 and 23 July 1975 at the BH site, with a few exceptions. As on the 16th, coal and coke were present at lower concentrations than on the 23rd, while the minerals were at higher concentrations. The titanium dioxide and hydrated iron oxide were present in nearly equal amounts and were the primary components of stages 5 and 6.

Municipal Court (98.2 $\mu g/m^3$)

When particles from this set of Andersen impactor substrates were compared to the 23 July 1975 samples at the MC site, there was almost no difference, even in mass loading. The types of particles present on the impactor stages and their distribution between the stages was the same except that ammonium sulfate crystals were only found on stage 7. Except for the ammonium sulfate particles, industrial sources contributed less than 1% of the total TSP.

ANALYTICAL RESULTS FOR WIND DIRECTIONS OTHER THAN SOUTHERLY

25 July 1975

Resultant Wind Direction:	30°
Resultant Wind Speed:	5.5 mph

The lowest TSP concentration at the MC site (41.2 $\mu g/m^3$) and the fifth highest TSP concentration at BH (131.3 $\mu g/m^3$) occurred on this date. The significant difference between the two TSP concentrations produced the lowest TSP ratio (MC/BH = 0.31) of any day.

Broadway and Hurck (131.3 $\mu g/m^3$)

Calcite particles were the major cause of high mass loadings on this hi-vol filter (Figure 25). Vehicle exhaust emissions were present in trace amounts.

Coal fragments with some coke particles were the industrial emissions with the greatest mass impact on this sample. However, as seen in the photomicrograph, coal and coke make up a much smaller portion of the sample than they did on the 23rd. Fly ash and ammonium sulfate are minor components of the sample, but their concentration is slightly higher than on the 23rd.

Titanium dioxide and hydrated iron oxides were trace sample components. Their presence was puzzling, however, since the wind on this date never extended more easterly than 50°. In addition, these oxides did not coat other, larger mineral grains, so they must not have been entrained by vehicles. This puzzle includes the coal and coke fragments, since they were present in too high a concentration compared to the flyash content to have been derived from coal burning. It appears that the wind direction at the International Airport may have differed from wind directions near the riverfront, which is less than ½ mile from BH.

Municipal Court (41.2 $\mu g/m^3$)

The northeast wind on this sampling day provided few aerosols other than those generated by automobile traffic. Calcium carbonate minerals composed at least 90% of the sample mass, while direct vehicle emissions provided most of the remainder. Traces of industrial emissions were present but they did not account for more than 2% of the mass; biological aerosols accounted for even less.

It was surprising that the TSP was so low at the downtown St. Louis site when the primary particle type, calcite, was the same as at the BH site, which had three times more TSP. The difference might simply be attributed to limestone stockpile emissions impact at BH, or perhaps emissions from cement manufacturing. The lower TSP at the MC site might, however, be traced to a park just to the north of MC, extending both east and west. This grassy area would not only reduce the amount of upwind traffic, but also serve as a settling basin.

24 July 1975

Resultant Wind Direction:	300°
Resultant Wind Speed:	5.7 mph

This sampling day was selected for analysis because it reported the lowest TSP concentration (57.3 $\mu g/m^3$) at the BH site. The MC site reported a slightly higher TSP concentration of 62.4 $\mu g/m^3$. No hi-vol filter was available for microscopical analysis from either site.

Broadway and Hurck (57.3 $\mu g/m^3$)

Stages 0-4 were almost entirely composed of minerals, primarily calcite. The modal size of particles on the stages ranged from 8 µm to 1 µm. Figures 26 and 27 show particles on stages 3 and 4, respectively. Approximately 1 to 5% of the samples were from industrial emissions--mostly coal and coke

fragments. Stage 0 showed a minor contribution from rubber tire fragments; otherwise, direct vehicle emissions constituted trace components. There were also traces of biological particulates and titanium dioxide and hydrated iron oxides.

Stage 5 was composed primarily of minerals: 5-10% were vehicle exhaust particles and 10-20% were coal fragments (Figure 28). Modal size was less than 1 μm.

Minerals, mainly calcite, were the primary sample component on stage 6. Calcite comprised 45-60% of the sample mass (Figure 29). [In general, the photomicrographs do not show this mineral dominance for stages 0-6. With microscope polarizers fully crossed, it is obvious that the mineral population is dominant. It is necessary to uncross the polarizers to show the opaque and isotropic particles which minimize the mineral presence. Figures 30 and 31 show the difference between the photomicrographs taken with crossed and with partially uncrossed polarizers.] Approximately 40-50% was carbonaceous tailpipe exhaust and 10-20% were industrial emissions, primarily coal fragments. Ammonium sulfate amounted to 1-5% of the mass. The modal size of the particles on stage 6 was less than 1 μm.

Ammonium sulfate was the primary sample component on stage 7 (Figure 32). As it was present as small crystals, it was not as readily visible as the large crystals formed on the samples collected on the 23rd. Minerals, automobile exhuast, and coal fragments made up most of the remaining mass. The back-up filter had a fine carbonaceous background with traces of most of the particulates found on the upper stages.

Municipal Court (62.4 $\mu g/m^3$)

Stages 0-4 were similar to each other and to the samples collected at BH on the same day. Minerals, primarily calcite, constituted 80-95% of the sample, with 1-5% coal fragments and flyash. Stage 0 contained 5-10% direct vehicle emissions: rubber tire fragments. Stage 1 also had some rubber tire fragments (1-5%) and the other stages showed trace amounts. Stages 2, 3, and 4 had traces of biological particulates. Stage 3 showed the typical dominance of mineral fragments (Figure 33). Stage 4 had 1-5% vehicle exhaust (Figure 34). The modal size of stages 0-4 decreased from 8 μm to 1 μm.

Stage 5 showed an increase in vehicle exhaust (Figure 35). Minerals still composed the largest portion of stage 5, 75-90%, while 5-15% were coal fragments. The modal size was less than 1 μm.

Stage 6 had 50-65% minerals, 25-40% vehicle exhaust particles, 5-15% coal fragments, and a trace of ammonium sulfate (Figure 36). The modal size was less than 1 μm.

On stage 7, 25-40% of the mass loading were industrial emissions from coal fragments and ammonium sulfate. The ammonium sulfate formed tiny crystals here instead of the large crystals seen in the samples from 23 July 1975; therefore they were not quite so obvious (Figure 37).

The back-up filter had a fine background of vehicle tailpipe exhaust with traces of minerals and industrial emissions.

22 July 1975

Resultant Wind Direction:	100°
Resultant Wind Speed:	4.2 mph

The samples from this date showed the highest TSP ratio (MC/BH = 1.09) of the samples available for microscopical analysis. Although the date reported the highest TSP ratio, the TSP concentration at MC (99.8 $\mu g/m^3$) was closest to the average TSP for this site (92.5 $\mu g/m^3$).

Broadway and Hurck (83.7 $\mu g/m^3$)

Even though the wind on this day was from the east (100°), the composition of the samples was very similar to those collected on the 24th when there was a northwest (300°) wind. The major difference was that stages 5 and 6 were lower in minerals (stage 6 had only 1-2% minerals) and higher in vehicle exhaust and coal fragments than the equivalent stages on the 24th.

Municipal Court (99.8 $\mu g/m^3$)

Though these samples were similar to those collected on the 24th, there were several important differences. Iron oxides of similar morphology to the hydrated iron oxides described in previous samples were present on stages 3-6. On stage 5 they composed 15-25% of the sample mass. These iron oxides must have originated in the east since the wind direction on the sampling day was easterly.

Ammonium sulfate was present as a larger sample component on stages 6 and 7 than on the 24th, the crystals being smaller on stage 6 and larger on stage 7. However, they never formed crystals as large as those collected on a day with a southerly wind.

SECTION 4

DISCUSSION

Ten of the 12 samples collected at the Broadway and Hurck (BH) site exceeded 75 $\mu g/m^3$ (Figure 38), compared to nine of the 12 samples at the Municipal Court (MC) site (Figure 39). Seven of the 12 sampling days produced higher TSP concentrations at BH. Six of these seven higher TSP days at BH were produced by resultant wind directions that were in the range of 160° to 220°. (The seventh higher TSP day occurred with a 30° resultant wind direction.)

Three of the six samples collected during southerly winds were analyzed microscopically. The sample collected 23 July 1975 at BH had the highest TSP of the study: 214.4 $\mu g/m^3$. The predominant source of the high TSP this day was coal and coke (60-75%), followed by minerals (15-25%) and titanium dioxide and hydrated iron oxides (5-15%). All but the minerals were clearly due to industrial emissions, which amounted to 65-90% of the total TSP. The small amount of flyash (≈0.5%) precluded the possibility that the source of the coal and pyrolyzed coal was boiler emissions. Rather, the flyash resulted from the production or use of coal and coke for some other purpose, such as metallurgical production.

The other two samples collected 15 July 1975 (126.5 $\mu g/m^3$) and 16 July 1975 (139.2 $\mu g/m^3$) with resultant wind directions of 190° and 160° respectively, showed significantly lower concentrations of coal and coke (≈15-25%) and much higher contributions from minerals (≈60-75%). These samples also showed an increase in rubber tire content, which suggests that these minerals (mainly calcite) were raised by traffic on paved and perhaps unpaved roads adjacent to the BH sampling site.

It is surprising that coal and coke also appeared at the BH site on 25 July 1975 when the resultant wind direction was 30°. Whereas the coal and coke content was approximately 5-15% and the flyash slightly higher (0.5-5%), the usual relative proportion was still inverted, suggesting that there is an additional coal and coke source to the northeast of BH. However, the major constituent of the high TSP was calcite (70-85%).

With the exception of the sample collected on 23 July 1975, all of the samples at BH and MC were predominantly calcite. The high TSP days at MC occurred with winds from the south, northwest, and east. Since calcite was the major cause of these high TSP concentrations the source of these calcite particles was probably fragments of paved road aggregate entrained by vehicles. This conclusion can be tested by evaluating the microinventory of both sites to

determine whether there were other sources of calcite that may have contributed to the high TSP.

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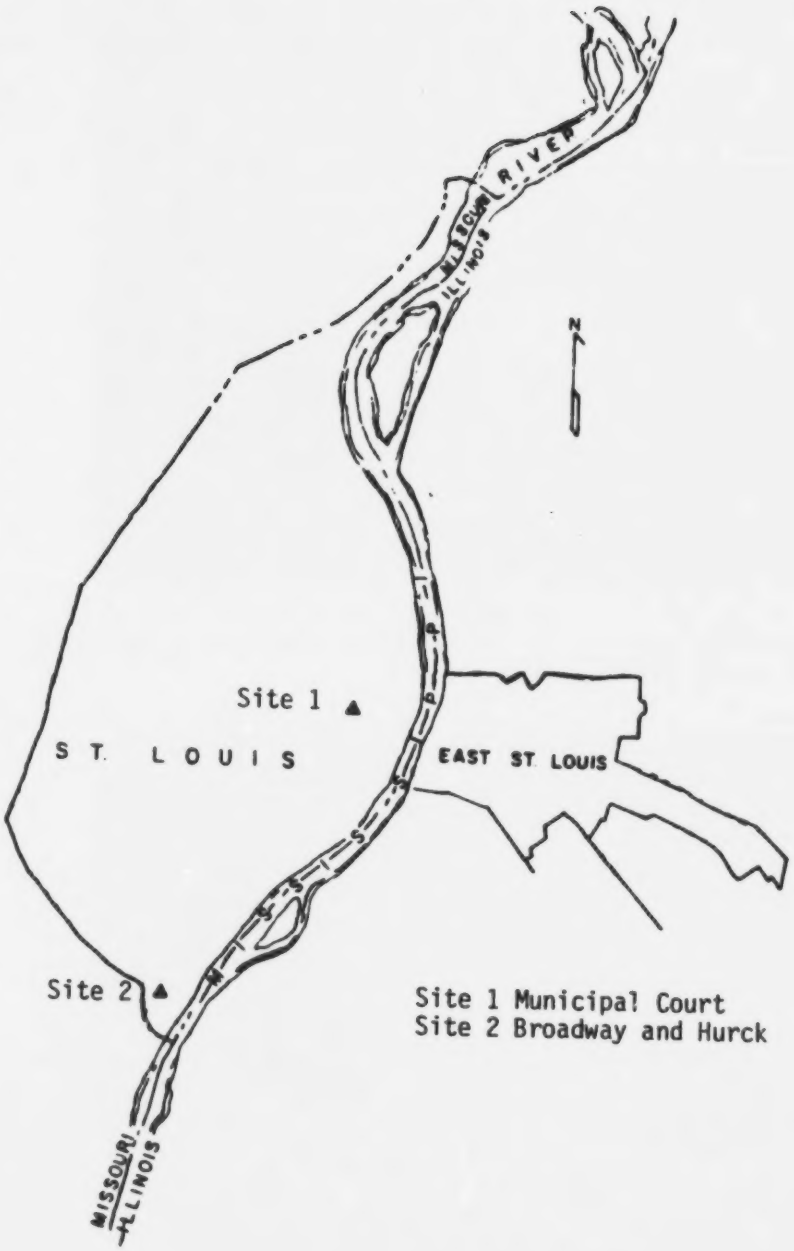

Figure 1. Sampling site locations.

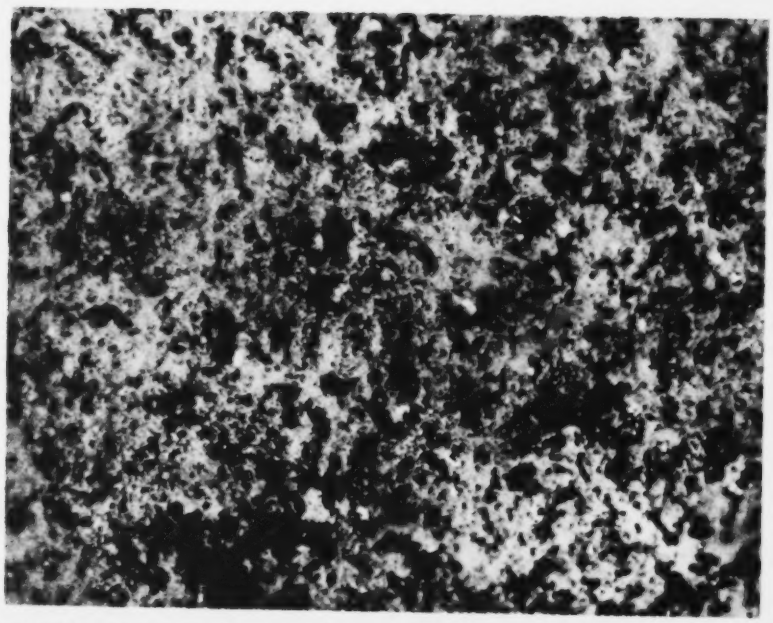

Figure 2. Photomicrograph of hi-vol collected at BH on 23 July 1975, showing heavy deposits of coke and coal; partially uncrossed polars (pup), 163X.

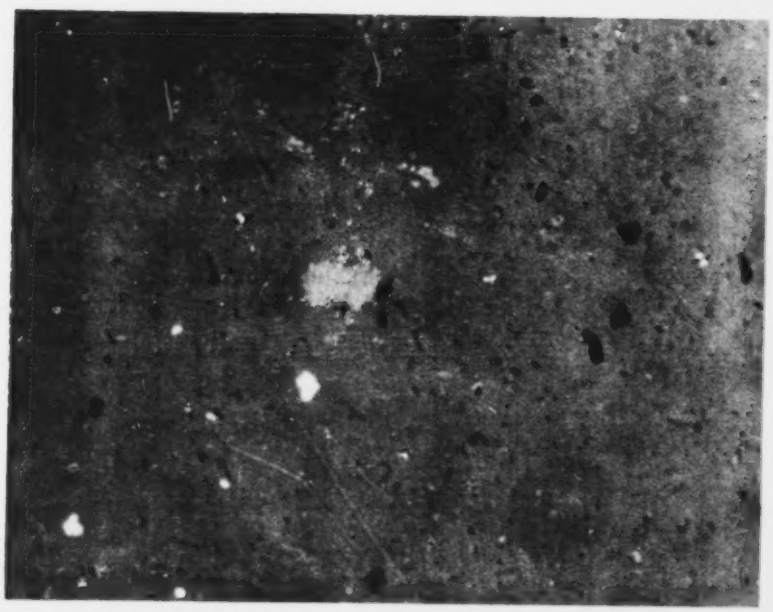

Figure 3. Photomicrograph of impactor stage 1 collected at BH on 23 July 1975, showing agglomerated submicrometer particles of hydrated iron oxide in the center of the figure; pup, 407X.

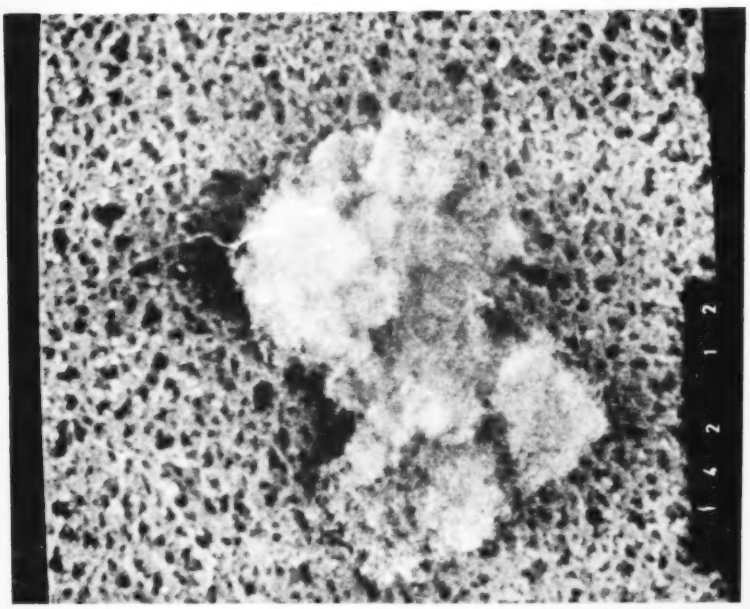

Figure 4. Scanning electron micrograph (SEMG) of submicrometer iron oxide agglomerate on impactor stage 1, collected at BH on 23 July 1975; 600X.

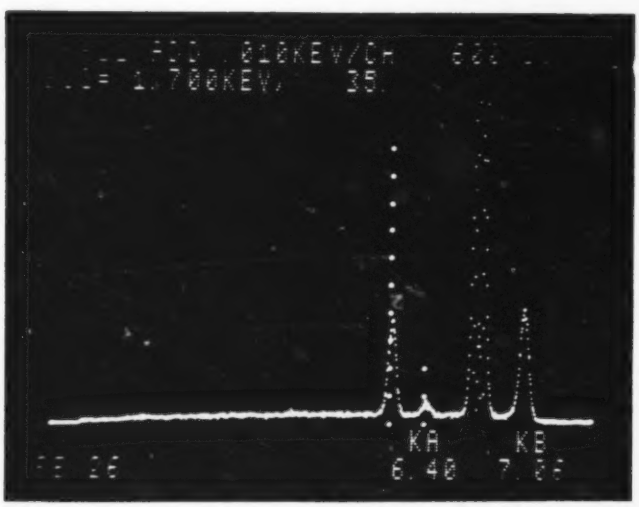

Figure 5. X-ray microanalysis of agglomerate in Figure 4, showing two peaks for iron and two for copper. The more intense copper peaks are caused by the copper sample holder.

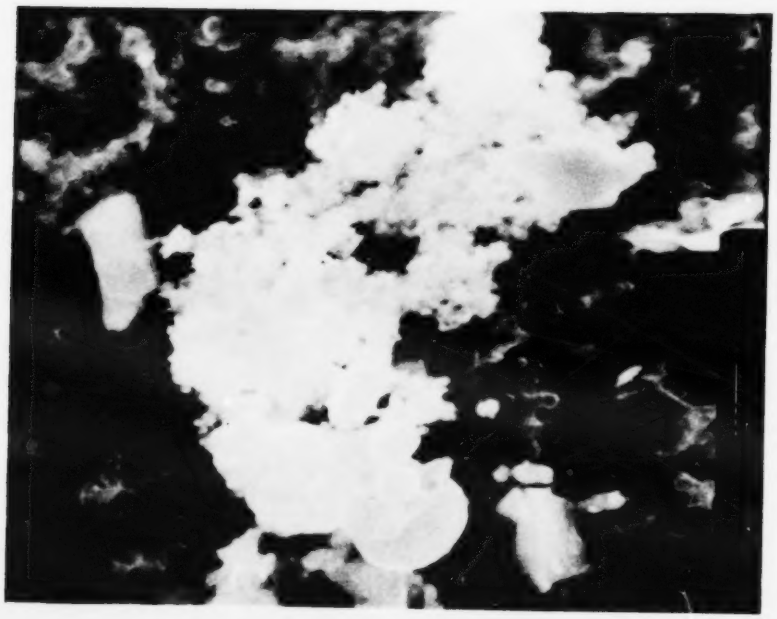

Figure 6. SEMG of submicrometer titanium dioxide agglomerate on impactor stage 2, collected at BH on 16 July 1975; 4,000X.

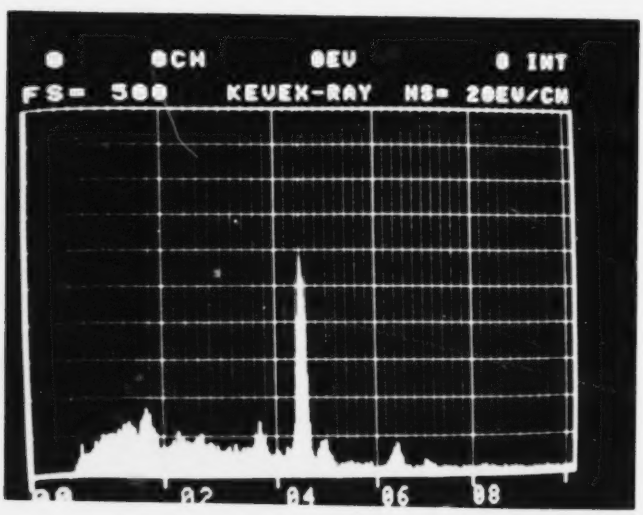

Figure 7. X-ray spectrum of agglomerate in Figure 6, showing a major peak for titanium plus trace to minor peaks for aluminum, silicon, sulfur, calcium, and iron from adjacent flyash particles.

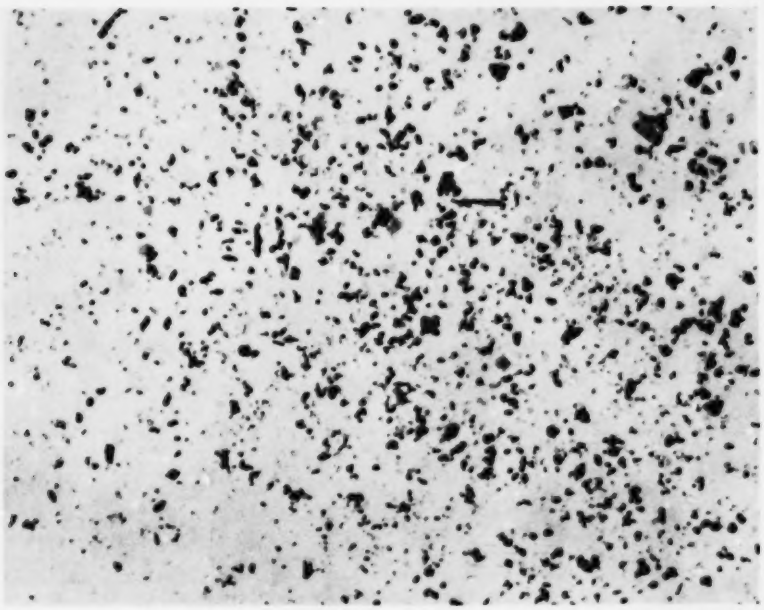

Figure 8. Photomicrograph of stage 2 impaction spot collected 23 July 1975 at BH; pup, 163X.

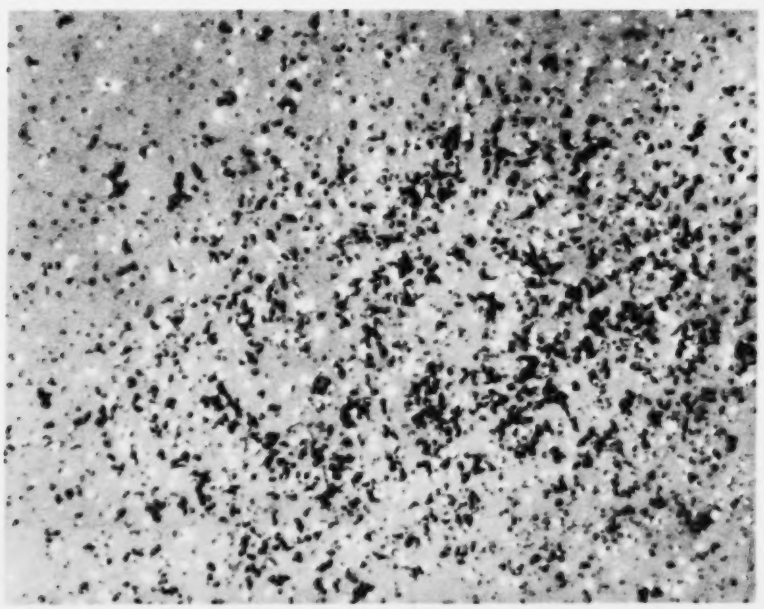

Figure 9. Photomicrograph of stage 3 impaction spot collected 23 July 1975 at BH; pup, 163X.

Figure 10. SEMG of a stage 2 impaction spot collected 23 July 1975 at BH; 160X.

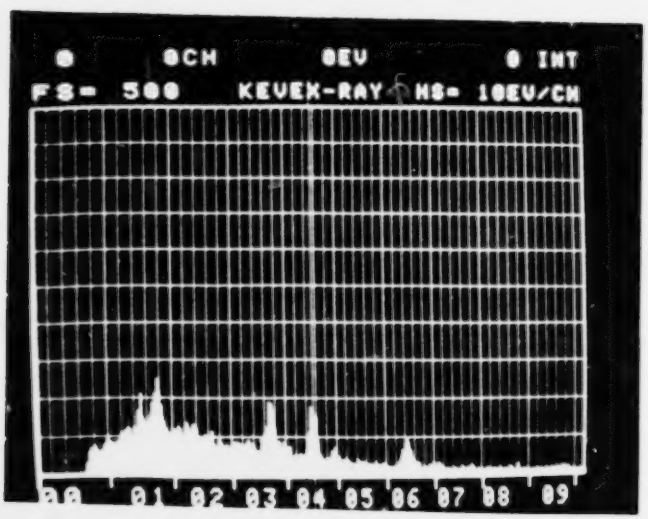

Figure 11. X-ray spectrum from analysis of the area shown in Figure 10 with peaks (left to right) for aluminum, silicon, calcium, titanium, and iron.

Figure 12. Photomicrograph of a stage 4 impaction spot collected 23 July 1975 at BH, showing a marked increase in coal and coke fragments; pup, 163X.

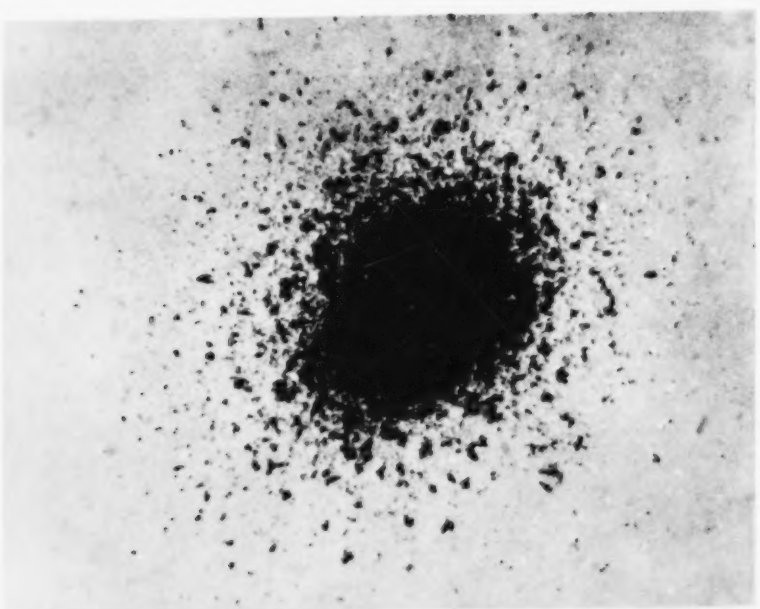

Figure 13. Photomicrograph of a stage 5 impaction spot collected 23 July 1975 at BH; pup, 163X.

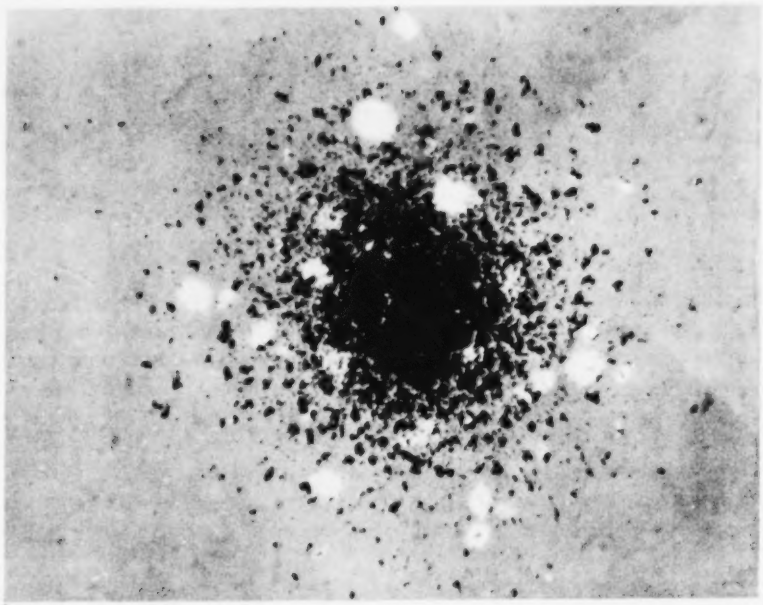

Figure 14. Photomicrograph of a stage 6 impaction spot collected 23 July 1975 at BH, showing large crystals of ammonium sulfate at the periphery of the main spot; pup, 163X.

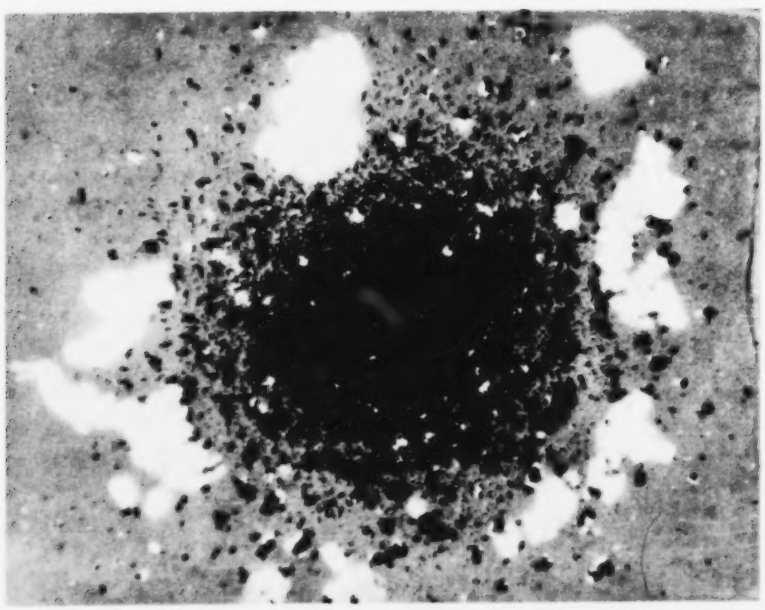

Figure 15. Photomicrograph of large crystals of ammonium sulfate found on impactor stage 7, collected 23 July 1975 at BH; pup, 163X.

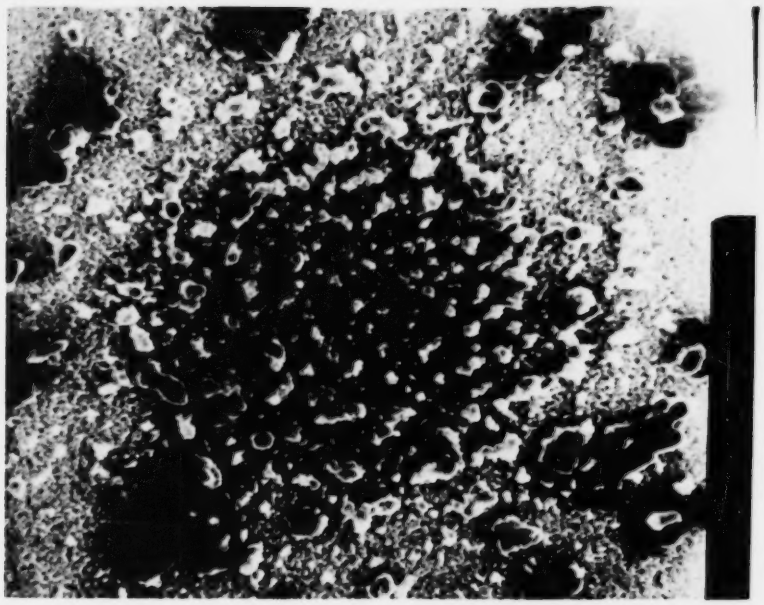

Figure 16. SEMG of a stage 7 impaction, collected 23 July 1975 at BH. showing a single impaction spot with large crystals of ammonium sulfate at the periphery; 200X.

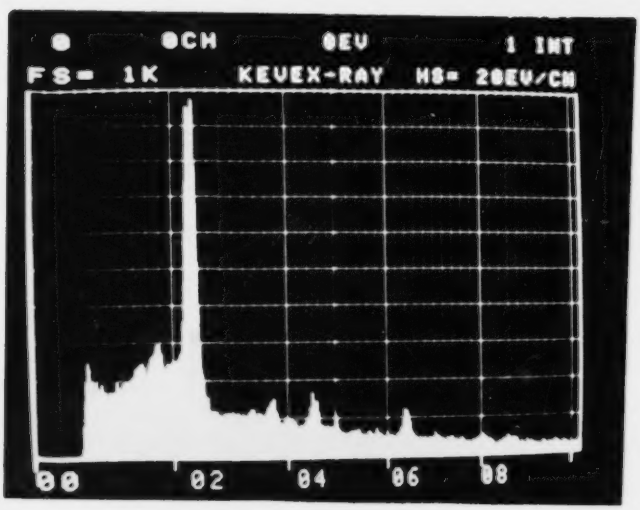

Figure 17. Area scan of the field of view in Figure 16, showing a major peak for sulfur with minor peaks for aluminum, silicon, potassium, calcium, titanium, iron, and copper. (The copper peak is probably an artifact from the sample holder.)

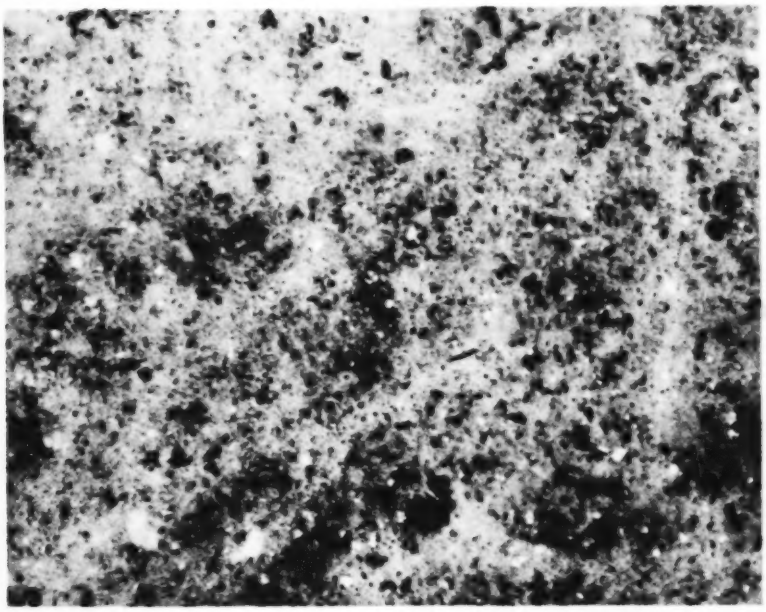

Figure 18. Photomicrograph of hi-vol collected 23 July 1975 at MC, showing bright white calcite particles and larger black fragments of coal and coke, along with submicrometer agglomerates of elemental carbon from vehicle exhausts.

Figure 19. Photomicrograph of an impaction spot from stage 2 collected 23 July 1975 at MC, showing (white) mineral particles that are principally calcite, with some quartz, feldspar, and mica; pup, 163X.

Figure 20. Photomicrograph of an impaction spot from stage 3 collected 23 July 1975 at MC; pup, 163X.

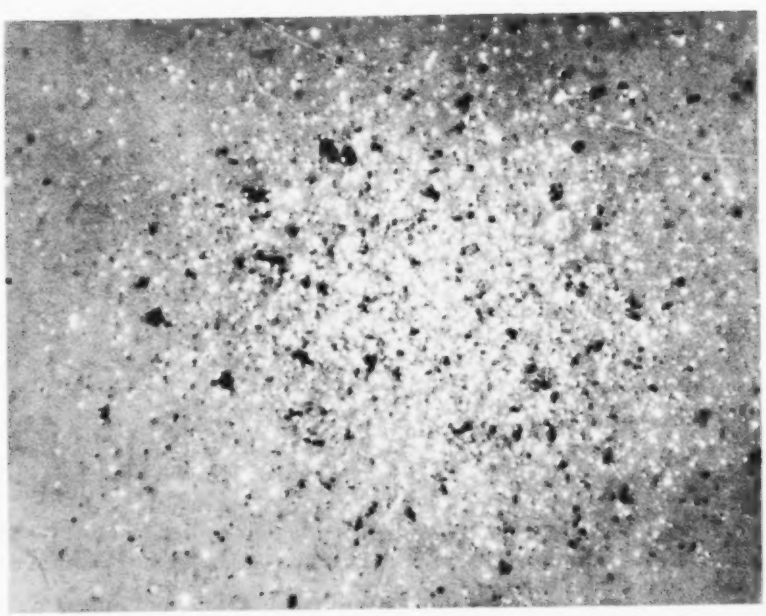

Figure 21. Photomicrograph of an impaction spot from stage 4 collected 23 July 1975 at MC; pup, 163X.

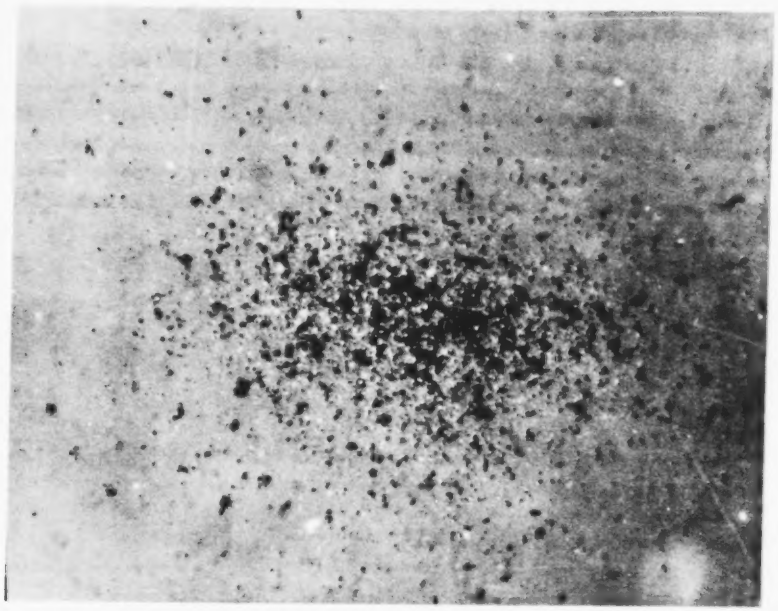

Figure 22. Photomicrograph of an impaction spot from stage 5 collected 23 July 1975 at MC; pup, 163X.

Figure 23. Photomicrograph of an impaction spot from stage 6 collected 23 July 1975 at MC, showing large recrystallized particles of ammonium sulfate, along with coal and coke fragments, minerals, and vehicle tailpipe emissions, which constitute the primary component on this stage; pup, 163X.

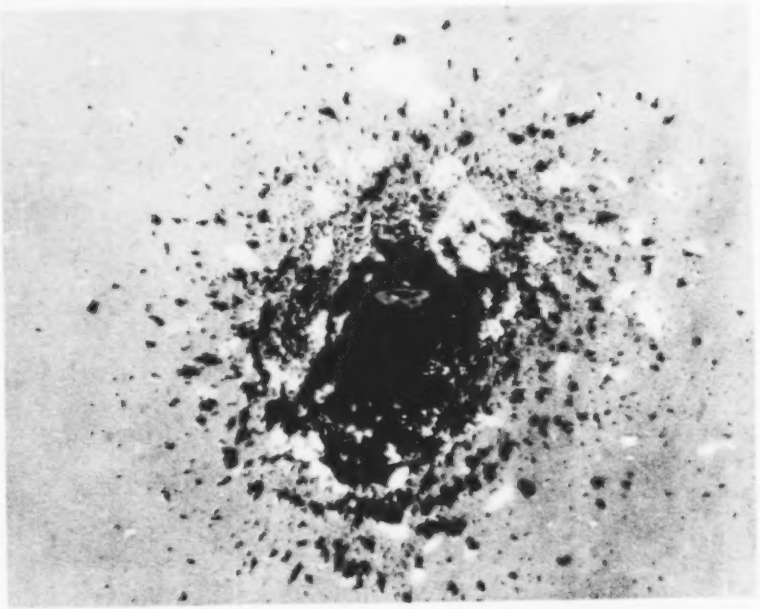

Figure 24. Photomicrograph of an impaction spot from stage 7 collected 23 July 1975 at MC, showing large recrystallized ammonium sulfate and vehicle exhaust particles; pup, 163X.

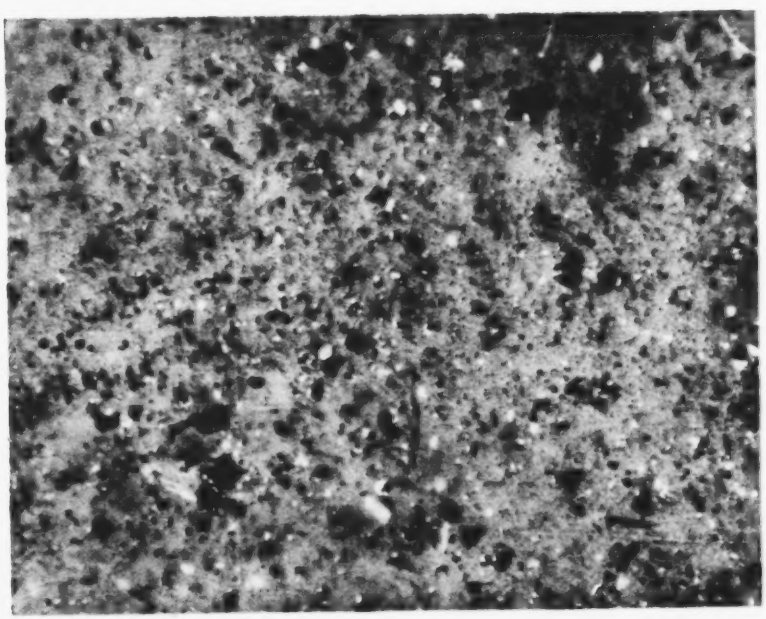

Figure 25. Photomicrograph of hi-vol collected 25 July 1975 at BH, showing mainly calcite and coal fragments; pup, 163X.

Figure 26. Photomicrograph of an impaction spot from stage 3 collected 24 July 1975 at BH, showing calcite and coal fragments; pup, 163X.

Figure 27. Photomicrograph of an impaction spot from stage 4 collected 24 July 1975 at BH, showing calcite and an increased coal fragment content over stage 3; pup, 163X.

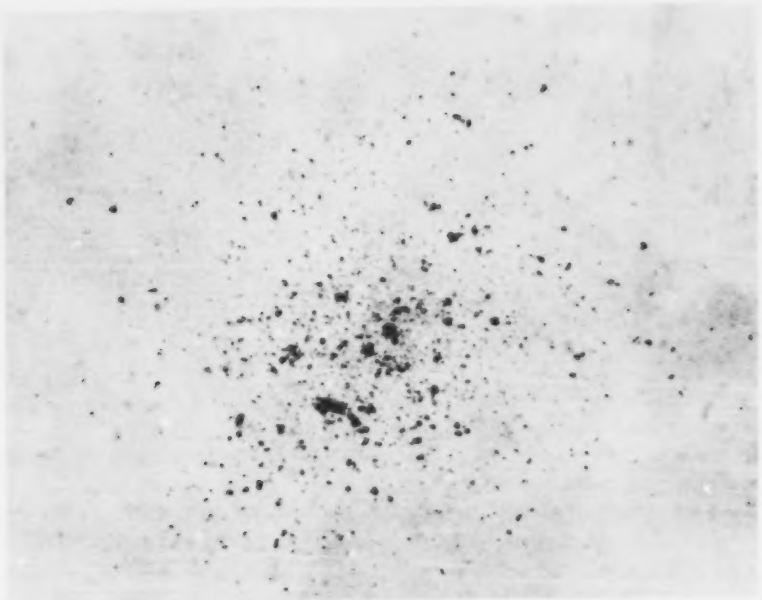

Figure 28. Photomicrograph of an impaction spot from stage 5, collected 24 July 1975 at BH, showing particles similar to those of stages 3 and 4; pup, 163X.

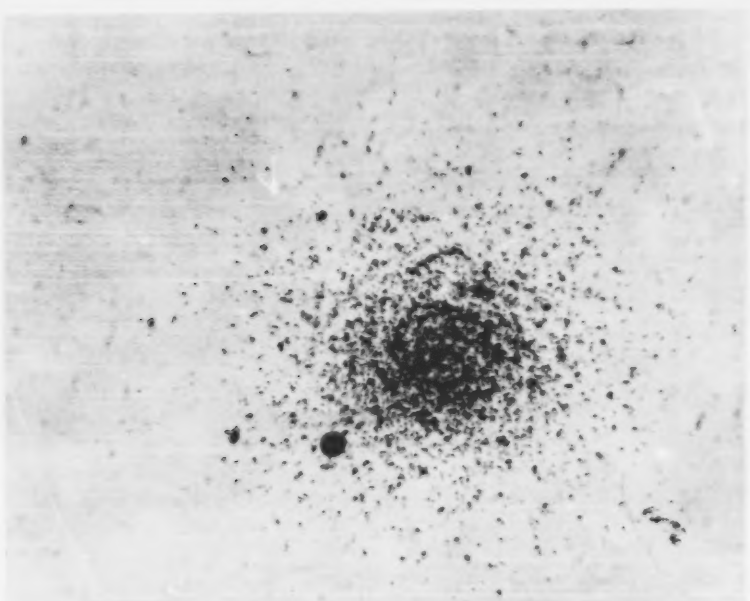

Figure 29. Photomicrograph of an impaction spot from stage 6, collected 24 July 1975 at BH; pup, 163X.

Figure 30. Photomicrograph of an impaction spot from stage 4, collected 23 July 1975 at BH, with partially uncrossed polarizers; 163X.

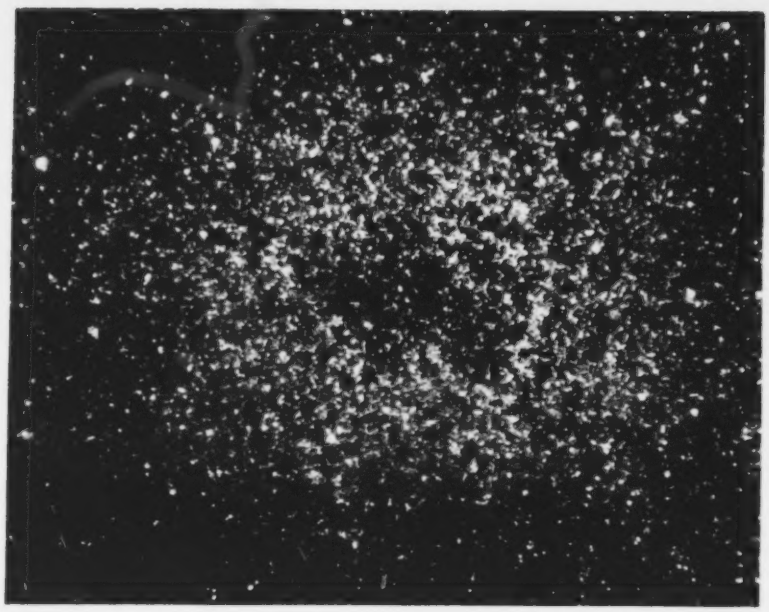

Figure 31. Same field view as shown in Figure 29 but with crossed polarizers; 163X.

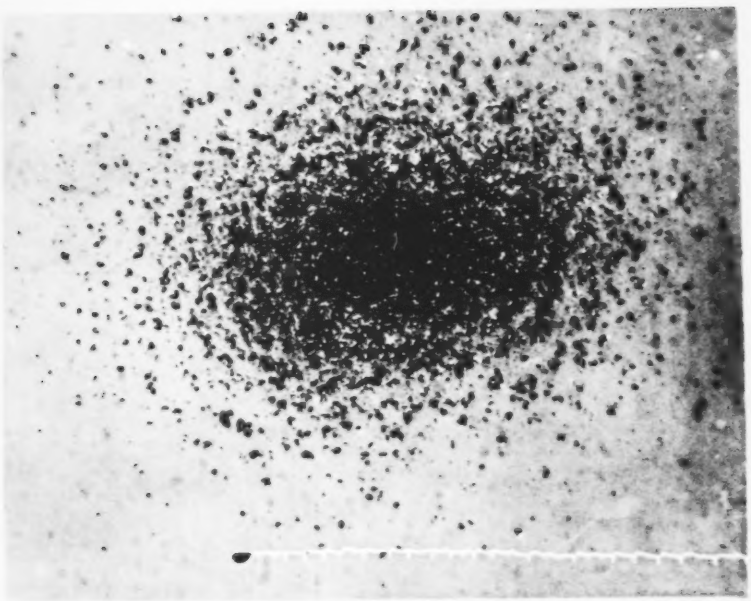

Figure 32. Photomicrograph of an impaction spot from stage 7, collected 24 July 1975 at BH, showing the presence of (white) ammonium sulfate crystals; pup, 163X.

Figure 33. Photomicrograph of an impaction spot from stage 3, collected 24 July 1975 at MC; pup, 163X.

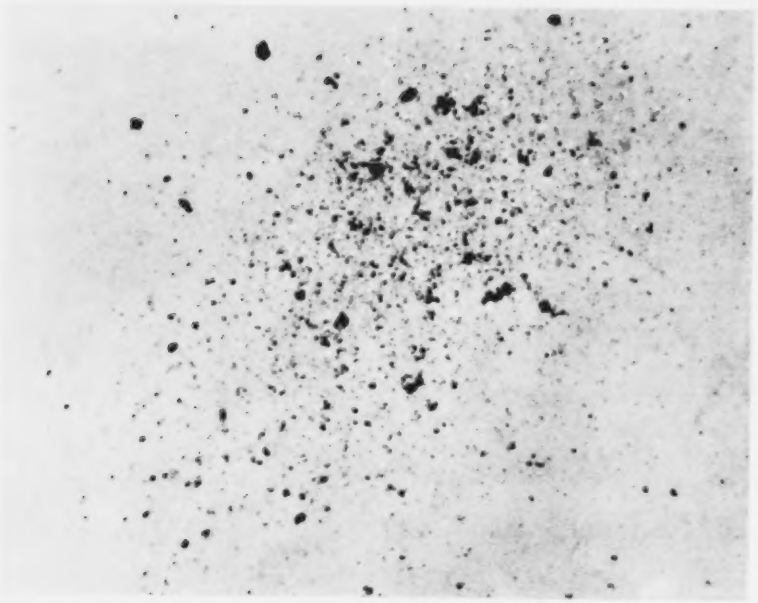

Figure 34. Photomicrograph of an impaction spot from stage 4, collected 24 July 1975 at MC; pup, 163X.

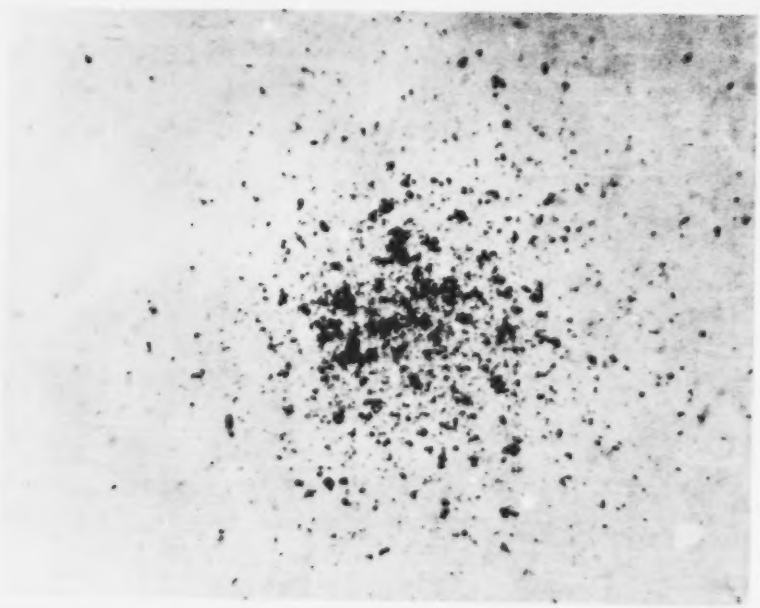

Figure 35. Photomicrograph of an impaction spot from stage 5, collected 24 July 1975 at MC; pup, 163X.

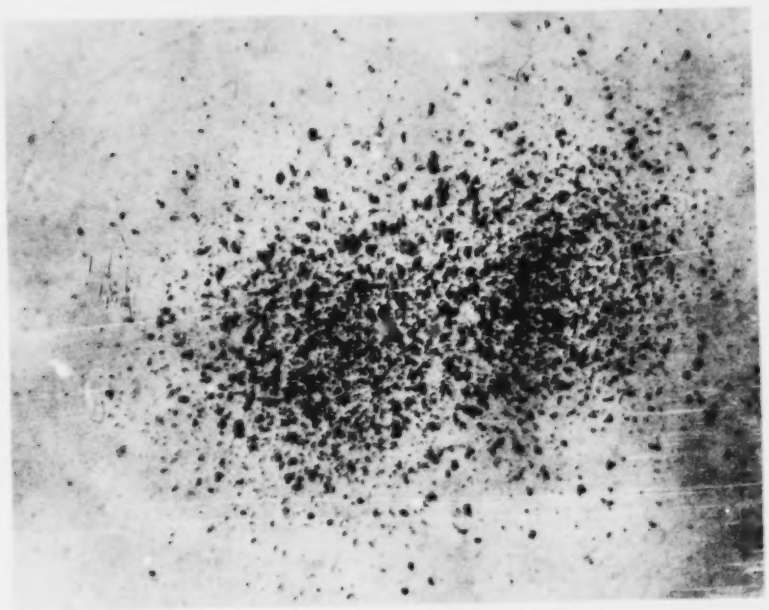

Figure 36. Photomicrograph of an impaction spot from stage 6, collected 24 July 1975 at MC; pup, 163X.

Figure 37. Photomicrograph of an impaction spot from stage 7, collected 24 July 1975 at MC; pup, 163X.

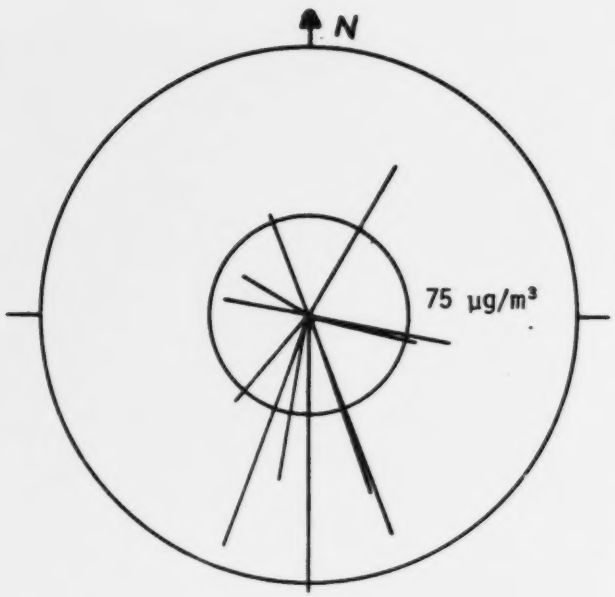

Figure 38. TSP rose for Broadway and Hurck hi-vol samples collected 15-26 July 1975.

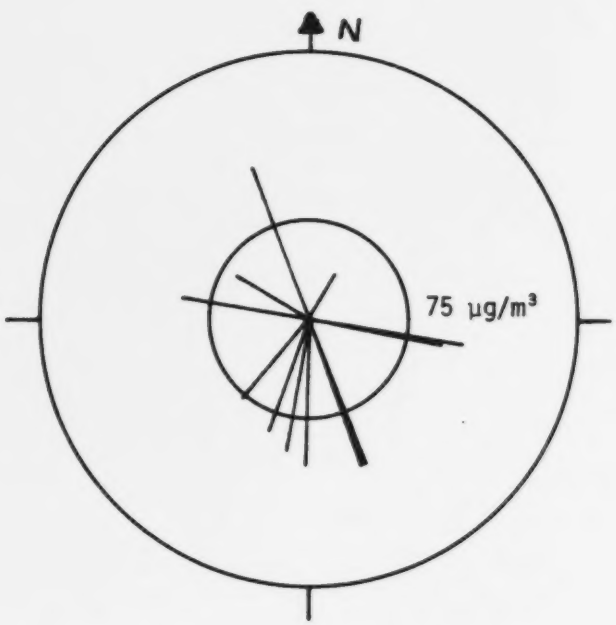

Figure 39. TSP rose for Municipal Court hi-vol samples collected 15-26 July 1975.